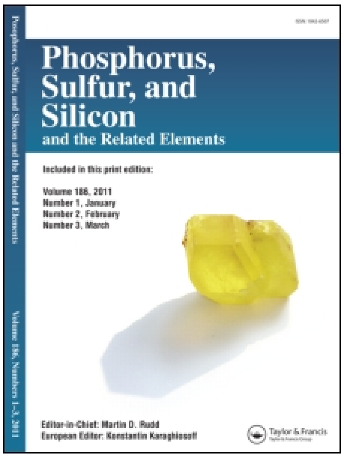

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A CONVENIENT SYNTHESIS OF LONG-CHAIN 3-n-ALKYLTHIOPHENES AND 3-n- ALKYLFURANS

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A CONVENIENT SYNTHESIS OF LONG-CHAIN 3-*n*-ALKYLTHIOPHENES AND 3-*n*-ALKYLFURANS

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The syntheses of 3-substituted long-chain furans and thiophenes by a Wittig reaction are described. ^{1}H-NMR and UV data of these compounds are reported.

Key words: 3-alkylfurans; 3-alkylthiophenes; 3-(alk-1-en-1-yl)thiophenes; 3-(alk-1-en-1-yl) furans; Wittig reaction; alkyltriphenylphosphonium bromides; long-chain alkylidenetriphenylphosphoranes; UV spectra; ^{1}H-NMR spectra.

INTRODUCTION

Though the high conductivity of polymers[1] derived of 3-methyl-[2–5] and 3-ethylthiophene[6,7] is known for some time, long-chain 3-*n*-alkylthiophenes have only rather recently been investigated for their electrochemical properties including conductivity. Thus, Sato *et al.*[8,9] reported on the synthesis by a Kumada coupling reaction[10] of a number of long-chain 3-alkylthiophenes including 3-*n*-octadecylthiophene. The polymerization and conductivity of these thiophenes have been described but no data, e.g. melting points, elemental analyses, and spectroscopical data have been reported for these compounds. Also the synthesis of long-chain 3-substituted thiophenes and pyrrols with oxygen and nitogen atoms in the substituent, their polymerization and electrochemical properties were recently communicated.[11,12,13]

In view of our continuous interest in such monomers and electrochemical properties of polymers derived of them, we synthesized a number of long-chain 3-*n*-alkylthiophenes and long-chain 3-*n*-alkylfuranes. The latter compounds were included due to our interest in the role played by the heteroatom on their electrochemical and spectral properties.[14]

RESULTS AND DISCUSSION

Though we[15] and others[16] recently prepared 3-*n*-alkylthiophenes with a chain length up to six atoms by a Kumada coupling reaction, this method failed in our

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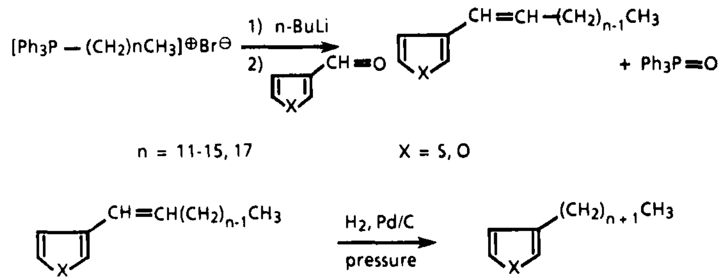


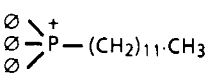
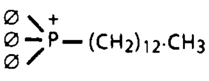
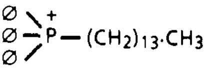
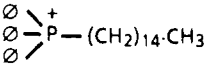
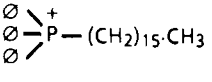
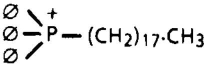
SCHEME I

hands to give good or even reproducible yields of the desired compounds. We therefore tried a number of alternative procedures[17] and settled eventually on the Wittig reaction for obtaining the desired compounds (Scheme I).

The alkyltriphenylphosphonium bromides **1–6** were obtained by reacting the appropriate alkyl bromide with triphenylphosphane in acetonitrile. The salts were difficult to obtain in crystalline form, however, their ^{1}H-NMR spectra agreed well with their structure (Table I).

TABLE I

$[Ph_3P - (CH_2)_nCH_3]^{\oplus}Br^{\ominus}$

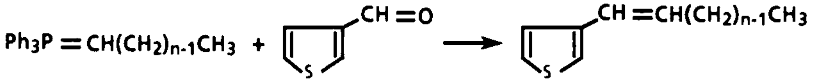
Alkyltriphenyl Phosphonium Bromides	No.	M.P. °C	^{1}H NMR ($CDCl_3$) δ (ppm)	Yield %
	1	*	7.6-8.1 (m, 15H, aromatic protons) 3.7 (m, 2H,$\underline{CH_2}$ attached to P), 3.1 (dd, 2H, P-$CH_2\underline{CH_2}$), 1.6(bs, 4H, 2 $\underline{CH_2}$), 1.2 (bs, 14H, 7 $\underline{CH_2}$) 0.9 (t, 3H, CH_3)	60
	2	*	7.5-8.1 (m, 15H, aromatic protons), 3.75 (m, 2H,P-$\underline{CH_2}$), 2.0 (bs, 2H, $CH_2\underline{CH_2}$), 1.6-1.2 (bs, 20H, 10 $\underline{CH_2}$) 0.9 (t, 3H, $\underline{CH_3}$)	82
	3	52	7.5-8.1 (m, 15H, aromatic protons), 3.7 (m, 2H,P-$\underline{CH_2}$), 1.9 (bs, 2H, $CH_2\underline{CH_2}$) 1.65-1.2 (bs, 2 bs, 22H, 11 $\underline{CH_2}$) 0.9 (t, 3H, $\underline{CH_3}$)	80
	4	53-4	7.6-8.1 (m, 15H, aromatic protons) 3.8 (m, 2H,P-$\underline{CH_2}$), 1.7-1.2 (bs, 2 bs, 26H, 13 $\underline{CH_2}$), 0.9 (t, 3H, $\underline{CH_3}$)	84
	5	*	7.6-8.1 (m, 15H, aromatic protons) 3.7 (m, 2H,P-$\underline{CH_2}$), 1.7 and 1.25 (2 bs, 28H, 14 $\underline{CH_2}$) 0.9 (t, 3H, $\underline{CH_3}$)	68
	6	101	7.6-8.1 (m, 15H, aromatic protons) 3.8 (b, 2H, P-$\underline{CH_2}$) 2.0-1.45 (b, 6H, 3 $\underline{CH_2}$) 1.2 (2 bs, 26H, 13$\underline{CH_2}$) 0.9 (t, 3H, $\underline{CH_3}$)	88

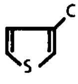
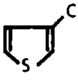
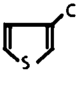
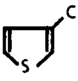
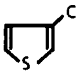
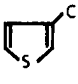
*non-crystalline wax-like solids

Deprotonation of the phosphonium bromides to the corresponding phosphoranes proceeded well with *n*-butyllithium. They were reacted with thiophene- or furan-3-carboxaldehyde at about 5°C. The reaction was terminated by quenching with a concentrated sodium chloride solution. The 3-(alk-1-en-1-yl)thiophenes and furans were purified by column chromatography and characterized by elemental analysis, MS, UV, and ^{1}H-NMR data (Tables II and IV), and chemically by reduction to the corresponding 3-alkylthiophenes or furans respectively (Tables III and V).

The λ_{max} of the UV spectra of the unsaturated thiophenes **7–12** are virtually identical; so are the positions of the λ_{max} of the analogous furans **21–24**; however

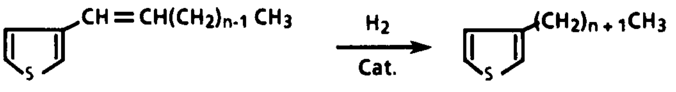
TABLE II

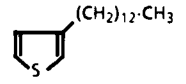
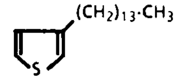
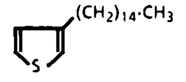
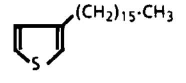
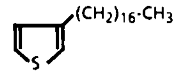
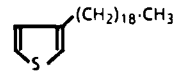


3-(Alk-1-en-1-yl)thiophene	No.	M.P	^{1}H NMR ($CDCl_3$) δ (ppm)	Elemental Analyses Calcd. C, H Found C, H	λ_{max} (nm) $CHCl_3$	Yield %
 $CH = CH(CH_2)_{10}{\cdot}CH_3$	7	*	7.2 (m, 3H, ring protons) 6.3 and 5.6 (2m, 2H, -CH = CH) 2.3 and 1.4 (m, bs, 20H, 10 $\underline{CH}_2$), 0.9 (t, 3H, $\underline{CH}_3$)	77.21 10.67 77.40 10.63	249	58
 $CH = CH(CH_2)_{11}{\cdot}CH_3$	8	•	7.2 (m, 3H, ring protons), 6.3 and 5.6 (2m, 2H, CH = CH) 2.3 and 1.4 (2bs, 22H, 11 $\underline{CH}_2$), 0.9 (t, 3H, $\underline{CH}_3$)	77.63 10.86 77.50 10.67	251	61
 $CH = CH(CH_2)_{12}{\cdot}CH_3$	9	*	7.2 (m, 3H, ring protons), 6.3 and 5.6 (2m, 2H, CH = CH) 2.3 and 1.4 (2bs, 24H, 12 $\underline{CH}_2$) 0.9 (t, 3H, $\underline{CH}_3$)	78.01 11.03 77.81 10.86	250	58
 $CH = CH(CH_2)_{13}{\cdot}CH_3$	10	•	7.0-7.3 (m, 3H, ring protons), 6.3 and 5.6 (2m, 2H, CH = CH) 2.2 and 1.35 (2 bs, 26H, 13 $\underline{CH}_2$), 0.9 (t, 3H, $\underline{CH}_3$)	78.36 11.18 78.12 11.07	250	56
 $CH = CH(CH_2)_{14}{\cdot}CH_3$	11	45	7.0-7.3 (m, 3H, ring protons), 6.4 and 5.7 (2m, 2H, CH = CH), 3.5 (m, 2H, $\underline{CH}_2$ attached to olefinic C), 1.5 (bs, 26H, 13 $\underline{CH}_2$), 0.9 (t, 3H, CH_3)	78.68 11.32 78.66 11.44	249	75
 $CH = CH(CH_2)_{16}{\cdot}CH_3$	12	40-1	7.2 (m, 3H, ring protons) 6.4 and 5.65 (2m, 2H, CH = CH), 2.2 and 1.4 (2bs, 32H, 16 $\underline{CH}_2$, 0.85(t, 3H, CH_3)	79.24 11.56 79.48 11.29	249	49

*non-crystalline wax-like solids

TABLE III



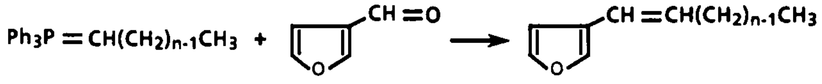
Reduction Products [3-Alkylthiophene]	No.	M.P. °C	^{1}H NMR ($CDCl_3$) δ (ppm)	Elemental Analyses Calcd. / Found C	H	λ_{max} (nm) $CHCl_3$	Yield %
	13	*	7.2 (dd, 1H, in position 5 of the thiophene ring), 6.9 (d, 2H, in position 2 and 4 in the thiophene ring), 2.6 (t, 2H, $\underline{CH}_2$ attached to thiophene ring), 2.3 (bs, 22H, 11$\underline{CH}_2$), 0.9 (t, 3H, $\underline{CH}_3$)	76.62 76.42	11.35 11.63	244	83
	14	*	7.2 (dd, 1H, 5 position in thiophene ring) 6.2 (d, 2H, in position 2 and 4 thiophene ring), 2.6(t, 2H, $\underline{CH}_2$ attached to thiophene ring), 2 and 1.3 (2bs, 24H, 12 $\underline{CH}_2$), 0.9 (t, 3H, $\underline{CH}_3$)	77.07 77.04	11.50 11.32	244	86
	15	*	7.2,6.9 (2m, 3H, thiophene ring), 2.6 (t, 2H,$\underline{CH}_2$ attached to thiophene ring), 1.7, 1.3 (2bs, 26H, 13$\underline{CH}_2$), 0.9 (t, 3H, CH_3)	77.48 77.56	11.63 11.60	245	68
	16	*	7.25 and 6.9 (2m, 3H, thiophene ring), 2.6 (t, 2H, $\underline{CH}_2$ attached to thiophene ring), 1.2 and 1.3 (2bs, 28H, 14 $\underline{CH}_2$), 0.9 (t, 3H, $\underline{CH}_3$)	77.85 77.60	11.76 11.67	244	72
	17	30	7.2 and 6.9 (2m, 3H, thiophene ring) 2.6 (t, 2H,$\underline{CH}_2$ attached to thiophene ring), 1.3 (2bs, 30H, 15 $\underline{CH}_2$), 0.9 (t, 3H, $\underline{CH}_3$)	78.19 78.37	11.87 11.64	244	50
	18	43	7.2 and 6.9 (2m, 3H, thiophene ring), 2.6 (diffuse t, 2H, $\underline{CH}_2$ attached to the thiophene ring), 1.2 (bs, 34H, 17 $\underline{CH}_2$), 0.9 (t, 3H, $\underline{CH}_3$)	78.78 78.90	12.07 12.07	242	64

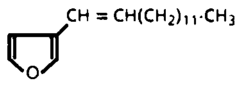
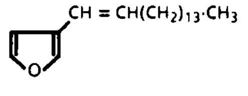
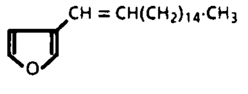
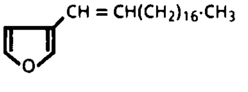
*non-crystalline wax-like solids

the latter ones show this peak shifted hypsochromically by about 4 nm. As expected the position of λ_{max} of the UV spectra of the saturated analogs **13–18** and **25–28** are practically the same.

The hydrogenation of the olefins was accomplished by shaking them in the presence of a 5% Pd/C catalyst under slight pressure in ethyl acetate solution. The process of the reaction was followed by monitoring the ^{1}H-NMR signals of the olefinic protons at δ 6.3–5.6 ppm. The hydrogenation was terminated when

TABLE IV



3(-Alk-1-en-1-yl)-furan	No.	M.P. °C	^1H NMR ($CDCl_3$) δ (ppm)	Elemental Analyses Calcd. C, H Found C, H	λ_{max} (nm) $CHCl_3$	Yield %
 $CH = CH(CH_2)_{11}\cdot CH_3$	21	*	7.4 (m, 2H, position 2 and 5 in furan ring), 6.45 (bs, 1H, position 4 in furan) 6.15 and 5.6 (2m, 2H, CH = CH) 2.15 (bs, 4H, 2 $\underline{CH_2}$), 1.4 (bs, 18H, 9 $\underline{CH_2}$), 0.9 (t, 3H, $\underline{CH_3}$)	82.38 11.52 82.18 11.63	247	36
 $CH = CH(CH_2)_{13}\cdot CH_3$	22	38	7.4 (m, 2H, position 2 and 5 in furan ring), 6.45(bs, 1H, position 4 in furan ring), 6.15 and 5.6 (2m, 2H, -CH = CH-), 2.15 (bs, 4H, 2$\underline{CH_2}$), 1.3 (bs, 22H, 11 $\underline{CH_2}$), 0.9 (t, 3H, CH_3)	82.69 11.80 82.48 11.64	245	39
 $CH = CH(CH_2)_{14}\cdot CH_3$	23	48	7.4 (m, 2H, position 2 and 5 in furan ring), 6.45(bs, 1H, position 4 in furan ring), 6.15 and 5.6 (2m,2H, -CH = CH-), 2.2(bs, 4H, 2 $\underline{CH_2}$), 1.3 (bs, 24H, 12 $\underline{CH_2}$), 0.9 (t, 3H, $\underline{CH_3}$)	82.83 11.92 83.00 11.76	244	33
 $CH = CH(CH_2)_{16}\cdot CH_3$	24	50	7.4 (m, 2H, position 2 and 5 in furan ring), 6.45 (bs,1H, position 4 in furan ring), 6.15 and 5.6 (2m,2H, -CH = CH-), 2.2 (bs, 4H, 2 $\underline{CH_2}$), 1.3 (bs, 28H, 14 $\underline{CH_2}$), 0.9 (t, 3H, $\underline{CH_3}$)	83.06 12.12 83.07 11.90	248	81

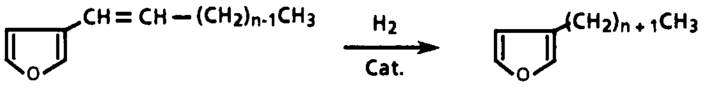
*non-crystalline wax-like solids

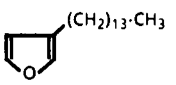
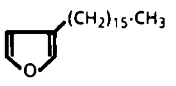
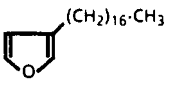
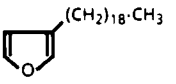
these signals disappeared. The yields of the 3-alkylthiophenes and 3-alkylfurans obtained by this procedure were generally good. The compounds were characterized by elemental analysis and ^{1}H-NMR spectra (Tables III and IV). The 3-alkylthiophenes and 3-alkylfurans obtained by this procedure were characterized by elemental analysis and ^{1}H-NMR spectra (Tables III and V).

EXPERIMENTAL

Melting points were determined with a Mel Temp apparatus and are uncorrected. UV spectra were run in $CHCl_3$ on the Perkin–Elmer Lambda 5 UV/VIS spectrophotometer. ^{1}H-NMR spectra were recorded at 80 MHz on an IBM, FTQ NMR spectrometer. Chemical shifts are expressed in δ (ppm) relative to tetramethylsilane as internal standard and $CDCl_3$ as a solvent. Elemental analyses were performed at M-H-W Laboratories, Phoenix, Arizona. All reactions were performed under N_2. Silica

TABLE V



Reduction Products [3-Alkylfuran]	No.	M.P. °C	^{1}H NMR ($CDCl_3$) δ (ppm)	Elemental Analyses Calcd. C, H Found C, H	λ_{max} (nm) $CHCl_3$	Yield %
	25	•	7.35 and 7.2 (2bs, 2H, in 2 and 5 position in furan ring), 6.2 (bs, 1H, in position 4 in furan ring), 2.35 (t, 2H, CH_2 attached to furan ring), 1.30 (s, 24H, 12 CH_2), 0.9 (t, 3H, CH_3)	81.75 12.19 81.99 11.66	244	80
	26	•	7.35 and 7.20 (2bs, 2H, position 2 and 5 in furan ring), 6.25 (bs, 1H, in position 4 in furan ring), 2.4 (t, 2H, CH_2 attached to furan ring), 1.3 (s, 28H 14 CH_2), 0.9 (t, 3H, CH_3)	88.12 12.41 81.93 12.70	244	83
	27	•	7.35 and 7.20 (2bs, 2H, in position 2 and 5 in furan ring), 6.25 (bs, 1H, in position 4 in furan ring), 2.4 (t, 2H, CH_2 attached to furan ring), 1.35 (s, 30H, 15 CH_2), 0.9 (t, 3H, CH_3)	82.28 12.50 82.43 12.31	244	90
	28	*	7.35 and 7.2 (2bs, 2H, in position 2 and 5 in furan ring), 6.25 (bs, 1H, in position 4 in furan ring), 2.4 (t, 2H, CH_2 attached to furan ring), 1.3 (s, 34H, 17 CH_2), 0.9 (t, 3H, CH_3)	82.57 12.65 82.32 12.56	243	85

*non-crystalline wax-like solids

gel 60 (Merck) was used for column chromatography and petroleum ether (b.p. 37–59°C) was used as an eluent. The reported yields refer to pure isolated materials. All the starting materials, bromoalkanes, thiophene-3-carboxaldehyde, and furan-3-carboxaldehyde are commercially available and were used without further purification.

General procedure for the preparation of ω-alkyltriphenylphosphonium bromides, **1–6**. The following procedure for the reaction of 1-bromododecane with triphenylphosphine is generally representative for the preparation of **1–6**.

A mixture of 1-bromododecane (9.72 g, 39 mm), triphenylphosphane (11.8 g, 45 mm) and acetonitrile (150 ml) was stirred magnetically and heated under N_2. After 36 h reflux time the solvent was evaporated on a rotary evaporator under reduced pressure. The residue which was a mixture of ω-alkyltriphenylphosphonium bromide and triphenylphosphane was purified by using a silica gel column. The mobile phase was first petroleum ether (37–59°C) and then diethyl ether. The phosphonium salt was eluted from the silica gel column by methanol. Evaporation of methanol gave 12 g of solid material (yield 60.15%).

However, the phosphonium bromides **1**, **2**, and **5** could not be crystallized and were isolated as viscous, transparent gums (Table I).

3-(Alk-1-en-1-yl)thiophenes, **7–12**. The preparation of compound **7** represents a typical example for the alkenes (**7–12**). In a three-necked nitrogen flushed, round-bottomed flask fitted with magnetic stirrer and septum, the phosphonium bromide **1** derived from 1-bromododecane (5.25 g, 12.18 mm) in dry THF (50 ml) was stirred magnetically under N_2, and cooled (ca. 5°C) in an ice bath. *n*-BuLi (1.6 M in hexane) (7.6 ml, 12.18 mm) was added dropwise by means of a syringe. The color of the reaction mixture changes to violet and then to orange-red. After 20 min, 1.12 g (10 mm) of 3-thiophenecarboxaldehyde in 10 ml THF were added slowly whereby the color of the reaction mixture turns from pale yellow to light brown. After removing the ice bath, stirring was continued overnight. Work-up was done by pouring the reaction mixture on conc. NaCl solution followed by extraction with diethyl ether. After drying over anhydrous $MgSO_4$, and distilling off the solvent, the material was purified by chromatography using a silica gel column and petroleum ether (37–59°C) as eluent to give 1.55 g of **7** (58.7%).

3-(Alk-1-en-1-yl)furans **21–24**. Preparation analogously to **7–12** (Table IV).

Synthesis of 3-alkylthiophenes **13–18**. The reduction of compound **12** is presented as an example for all other reductions of the olefins **7–12**.

A solution of compound **12** (1.044 g, 3 mm) in ethyl acetate (50 ml) was hydrogenated in the presence of 5% Pd/C (500 mg) as a catalyst for six h under 40 lbs/sq inch of H_2-pressure. The mixture was filtered and the solvent removed. The product was purified by column chromatography using silica gel and petroleum ether (37–59°C) as eluent to give 0.87 g of **18** (65.5%) (Table III).

3-Alkylfurans **25–28**. The preparation of the 3-alkylfurans was performed in the same manner as described for **13–18**, except that the pressure used was only 20 lbs/sq. inch (Table V).

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